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Abstract

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COMPARATIVE STUDY OF CHEMICAL RIPENING AND PHOTOLYSIS OF PHOTOGRAPHIC EMULSIONS

In order to clarify the interrelation and the features of the mechanism of topochemical and photochemical transformations that determine the quality of a photographic image, their comparative experimental study by methods of direct observation is of interest. The literature describes the results of such studies which, however, did not aim at comparing these processes. From the published works, nevertheless, some conclusions important for further study may be drawn, namely:

1. The speck centers arising during chemical ripening are, in all probability, silver in nature and form an aggregate of particles of different sizes, differing in their functions (^1).
2. The overwhelming amount of photolytic silver is formed within the volume of the microcrystals, whereas only a small part of it, detectable only in the region of solarization, is concentrated on their surface (^2).
3. Photolytic silver is liberated at the initial stage of exposure in the form of particles of molecular-colloidal dispersion, the presence of which is characterized by the fine structure of the impurity absorption spectrum (^3).
4. The course of the photolysis curves in the initial stage is similar to the characteristic curve (after development of the latent image), which, however, is shifted toward increasing exposures (^4, ^5).
5. The optical densities of a latent image created by actinic light, upon irradiation with red light, at first decrease and then begin to increase, which gives rise to the assumption of a coagulation mechanism for the evolution of silver centers (^6).

In the present work, a photometric method was used to study transformations in a silver iodide-bromide emulsion during chemical ripening and in Lippmann silver bromide emulsion during photolysis. In order to distinguish surface and internal transformations, oxidation of the layers was employed, which destroyed the surface centers. In parallel, during the chemical ripening of the silver iodide-bromide emulsion, changes in its photographic properties were studied; in the

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

case of the Lippmann emulsion, optical densities were also measured after development in order to construct the characteristic curve.

The optical densities in the study of chemical ripening were measured in different spectral regions on an SF-4 spectrophotometer, and in the case of photolysis on Kirillov' s apparatus with an integrating sphere at $\lambda = 710$ mμ. Before photometry, the layers of the silver iodide-bromide emulsion were desensitized with pinacryptol yellow $(1:10^4,\ 3\ \text{min})$.

The results obtained are illustrated in Figs. 1 and 2, which present experimental data in the form of curves of change in optical density, on the one hand, with time of chemical ripening for surface and internal transformations and, on the other, as a function of exposure for total and surface photolysis. In order to reveal—

the interrelations and regularities, the indicated curves are compared, respectively, with the change in the photographic properties of the silver iodobromide emulsion and with the curve after development of the Lippmann emulsion. On examining these results it is easy to detect a similar course of the photolysis curves and of the surface topochemical transformations in the initial stage of ripening (up to 16 hours). At the same time, both dependences do not exhibit a monotonic change in optical densities.

The similarity of the dependences considered suggests, it would seem, a fundamental similarity of the chemical transformations underlying both processes, namely their reduction-oxidation nature. At the same time, the absence of monotonicity in the change of optical densities indicates the existence, parallel to the accumulation of reaction products of free silver, of side processes that determine the evolution of silver centers. The observed picture makes it possible to conclude that, together with the formation of the simplest silver particles—primary centers—there occurs their growth and a decrease in their number. In the initial period of rapid accumulation of primary centers the light absorption increases, and with the subsequent decrease in their number the absorption also decreases. Since the decrease in the number of primary centers is accompanied by an increase in the number of secondary centers, from a certain moment the optical density begins to rise again.

Fig. 1. a —photosensitivity S and fog density D_0; b —impurity absorption of surface centers ΔD_{pov}; c —impurity absorption of internal centers ΔD_{vn}; t_2 — time of the second ripening

Fig. 2. 1 –total photolysis, 2 –photolysis on the surface of microcrystals (difference between the total curve and the curve after oxidation of surface silver), 3 –photolysis after dissolution of silver halide (fixing in an alkaline solution), 4 –characteristic curve (after development and fixing)

It is also seen from Fig. 1 that, on the one hand, there is a coupled change in the values of photosensitivity and absorption of surface centers at the —

initial stage of their evolution, and, on the other, of the fog density and absorption of the same centers, but at a later stage.

Such an interrelation indicates a direct dependence of photosensitivity on primary centers, and of fog on secondary centers, since among the latter catalytically active centers initiating development must be formed. The latent-image centers also belong to the secondary centers, as is indicated by the position of the characteristic curve in comparison with the photolysis curve (see Figs. 2, 4 and 1, respectively).

During chemical ripening and photolysis, transformations occur not only on the surface of the emulsion microcrystals, but also in their internal defects. Internal transformations are apparently promoted by gelatin located in defects and retained at the stage of the crystallization process. It is characteristic here that the total effect of internal transformations exceeds the surface ones. Under the action of light, an increase in optical densities due to surface transformations is observed only under deep photolysis, which agrees with Meidinger’ s data (2). The existence of internal transformations is confirmed by changes in the depth photosensitivity during chemical ripening (7).

As for the mechanism of chemical and photochemical reduction, here, in all probability, there is a complex coexistence of various elementary processes. The accumulation of the simplest silver particles observed at the initial stage of chemical ripening and photolysis indicates, above all, the participation in the reduction process of mobile (weakly bound to the lattice) silver ions. Further coarsening of the particles may be accomplished in two ways: on the one hand, by redistribution of silver with the participation of thermal dissociation of small particles and growth of large ones, and on the other, by particle growth first according to Mitchell’ s scheme (8):

$$\mathrm{Ag}_n + \mathrm{Ag}_0^+ + \bar{e} \to \mathrm{Ag}_{n+1}^+ + \bar{e} \to \mathrm{Ag}_{n+1},$$

then according to the Gurney-Mott scheme (9):

$$\mathrm{Ag}_m + \bar{e} + \mathrm{Ag}_0^+ \to \mathrm{Ag}_m^- + \mathrm{Ag}_0^+ \to \mathrm{Ag}_{m+1},$$

where $m > n$. Some data from studies of the luminescence of silver chloride emulsions indicate the coexistence of both mechanisms (10).

Thus, one may draw the general conclusion that there is a fundamental similarity of the chemical transformations in the processes of chemical ripening and photolysis, consisting in the reduction-oxidation nature of these processes. Since, moreover, the third stage of the photographic process—development—undoubtedly has the same nature, one may speak of the chemical unity of the photographic process as a whole.

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